THERMAL EXPANSION AND SOME PROPERTIES OF $CoSb_3$, $RhSb_3$ and $IrSb_3$

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Abstract

$IrSb_3$ and the isostructural compounds $RhSb_3$ and $CoSb_3$ were recently identified as new" promising thermoelectric materials (Caillat ct al. 1993a). The usc of these materials in thermoelectric devices requires that their properties shall not change over long periods of time at operation temperature. Temperature stability of the compound $IrSb_3$ was evaluated by recording the changes in weight and electrical resistivity of an $IrSb_3$ sample as a function of time. Information about the thermal expansion coefficients of the thermoelectric materials arc also of interest for the practical realization of the device. Thermal expansion coefficient of $IrSb_3$ and $RhSb_3$ were measured by high temperature X-ray study and were found to bc 7.96 x 10^{-6}/C (25-500 *C) for $IrSb_3$ and 12.7 x 10^{-6}/C (25-500°C) for $RhSb_3$. The thermal expansion coefficient of $CoSb_3$ was measured using a conventional dilatometer apparatus and was found to bc 13,46 x 10^{-6}/C (25-450* C).

INTRODUCTION

A broad search for ncw high temperature thermoelectric materials conducted at the Jet Propulsion Laboratory led to the discovery of new compounds with remarkable thermoelectric properties: $IrSb_3$, $RhSb_3$ and $CoSb_3$ (Caillat at al. 1993 b). The structure of these compounds is of the skutterudite, $CoAs_3$ type. This structure is composed of a cubic lattice of metals atoms and four-membered planary rings of non-metal atoms. An obvious requirement of a thermoelectric material is that it must bc stable at the temperature of operation. In our recent study of the phase diagram of the Ir-Sb systcm (Caillat ct al. 1993c), the peritectic decomposition temperature of $IrSb_3$ was determined at 1141°C but, because of the relatively low melting point of antimony (632°C), the vapor pressure of the compound might not bc negligible at high temperature closc to the peritectic decomposition temperature and partial dissociation might occurred, We recently started to investigate the temperature stability of these compounds. Preliminary results of long-term stability of the compound $IrSb_3$ are presented in this paper,

Little information is available on thermal expansion of $IrSb_3$, $RhSb_3$ and $CoSb_3$. A thermal expansion coefficient of 8.0 x 10^{-6}/C (20-432 *C) was determined for $IrSb_3$ by high temperature X-ray study (Kjekshus 1961) but no measurement of the coefficient for $RhSb_3$ and $CoSb_3$ can bc found in the literature. The thermal expansion coefficient of the compounds $IrSb_3$, $RhSb_3$ and $CoSb_3$ were determined by high temperature X-ray studies and also by conventional dilatometry technique.

EXPERIMENTAL

Long-term temperature stability of $IrSb_3$ was estimated by recording the variations of the electrical resistivity and the weight of a sample heated in vacuum over long periods of time. The electrical resistivity of a sample about 2 mm thick and 6 mm in diameter was measured by Hall effect. A Siemens D-500 Diffractometer equipped with a vacuum hot-stage was used to measure the lattice constant changes with temperature for the powdered $IrSb_3$ and $RhSb_3$ samples. The incident X-ray was CuK_α and the detector was a NaI scintillator with a graphite monochromator. X-ray scans were taken at 100°C intervals up to 1000°C for $IrSb_3$ and to 700°C for $RhSb_3$. The platinum diffraction was recorded at each temperature for calibration, Above 500°C, the position of the diffraction lines was very diffused, calculation of the lattice constant became uncertain and data were not retained.

RESULTS AND DISCUSSION

The lattice constant of the compounds $IrSb_3$ and $RhSb_3$ arc plotted as a function of temperature in Figure 1, The lattice constant increases linearly with the temperature for both compounds. The relative change in the length of the lattice constant is similar for both compounds.

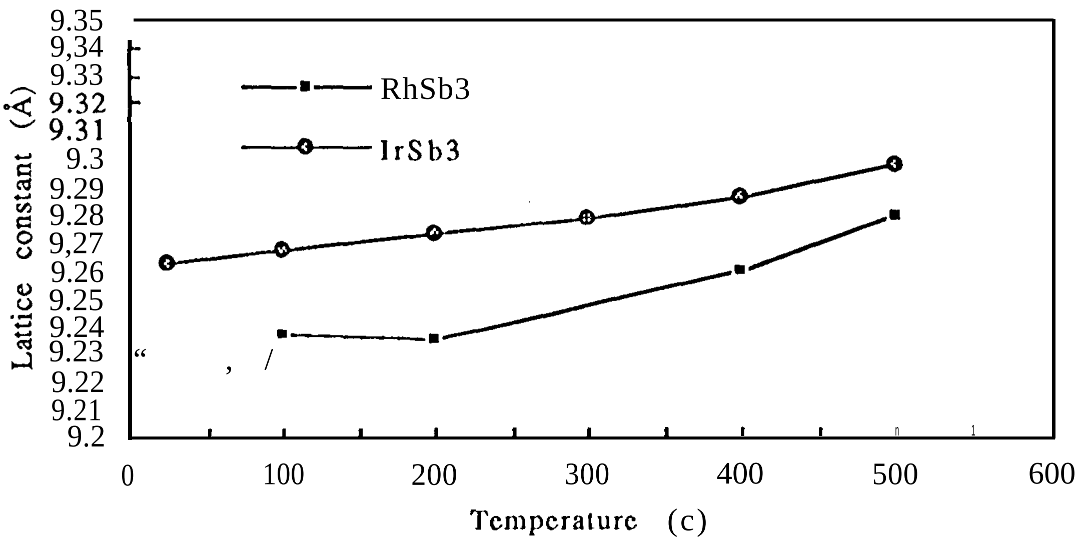

FIGURE 1. Lattice Constant versus Temperature for $RhSb_3$ and $IrSb_3$.

The relative lattice constant variations were calculated and plotted for the compounds $RhSb_3$ and $IrSb_3$ in Figure 2. For the compound $IrSb_3$, a linear variation is observed between room temperature and 500 'C. The expansion coefficient is equal to 7.96 x 10^{-6}/C between 25 and 500°C. This value agrees very well with the value of 8.0 x 10^{-6}/C (20-432°C) found in the literature (Kjekshus 1961). For $RhSb_3$, the data arc more scattered and the thermal expansion coefficient was estimated at 12.7 x 10^{-6}/C between 25 and 500°C. Using a conventional dilatometry technique, a thermal expansion coefficient of 13.46 x 10^{-6}/C was measured on a $CoSb_3$ sample between 25 and 450°C. The room temperature lattice constant of the compounds $IrSb_3$, $RhSb_3$ and $CoSb_3$ arc 9.26, 9.22 and 9.03 Å, respectively. In this family of compounds, the thermal expansion coefficient increases with decreasing lattice constant.

The weight changes of an $IrSb_3$ sample heated under vacuum at 500°C arc plotted in Figure 3. After 250 hours, a slight change in weight was observed likely duc to sornc

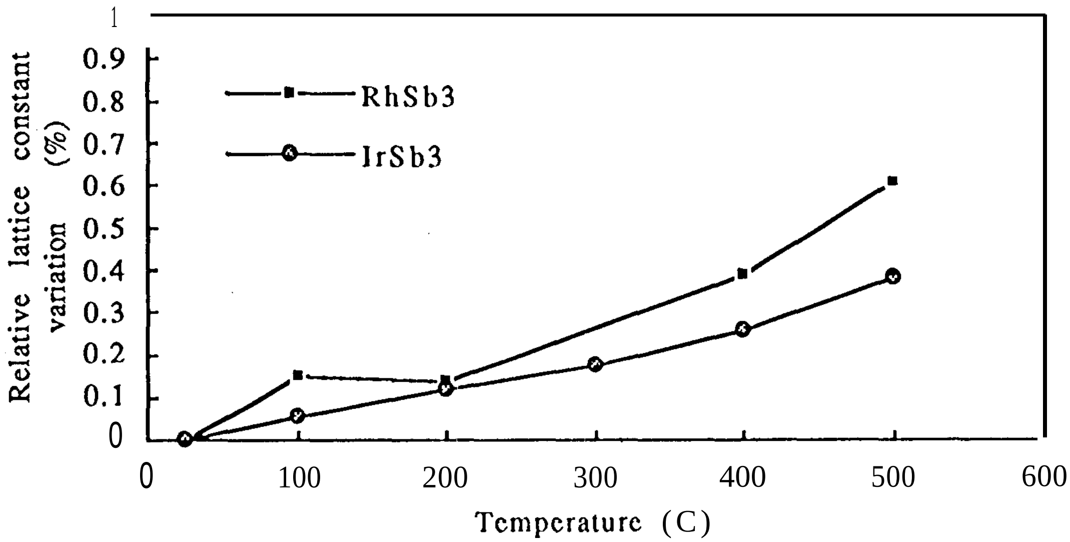

FIGURE 2. Relative Lattice Constant Variation versus Temperature for $RhSb_3$ and $IrSb_3$.

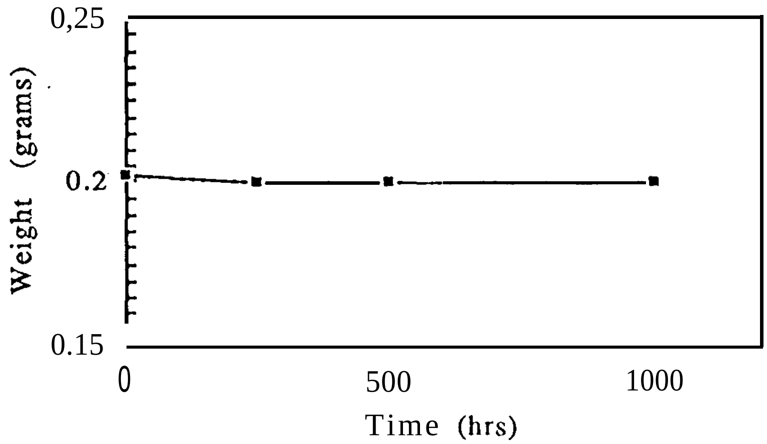

FIGURE 3. Weight variation of $IrSb_3$ Sample Heated at 550°C.

changes of the stoichiometry. No further changes were observed for times up to 1000 hours. This test is currently being continued. The stability of the compound at 500°C was also demonstrated by recording changes in the electrical resistivity of the sample as a function of the time, Indeed, besides a slight change in the electrical resistivity of the sample observed after 250 hours, consistent with the change in weight, no further change was observed up to 1000 hours. This test shows that $IrSb_3$ should be stable for temperatures at least up to 500 "C. These tests will be continued and the stability of $IrSb_3$ at higher temperature will also be investigated.

CONCLUSION

We measured the thermal expansion coefficient for the compounds by X-ray powder method and also conventional dilatometry technique. $IrSb_3$ was found to be stable at a temperature of 500°C over long period of time by recording changes in the weight and electrical resistivity of a sample, The temperature stability tests will be continued and different temperature will be investigated.

Acknowledgments

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